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No. 4

"Porphyroxine-Meconidine" in Relation to the Origin of Opium

In continuation of the international programme of scientific research undertaken pursuant to Resolution 246 F (IX), adopted by the Economic and Social Council on 6 July 1949, the Secretary-General is now publishing the present paper, which gives data on the "porphyroxine-meconidine" content of the United Nations opium samples, and conclusions from all the data now available as to the relation between the "porphyroxine-meconidine" content and the origin of the opium.

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"PORPHYROXINE-MECONIDINE" IN RELATION TO THE ORIGIN OF OPIUM

I. Introduction

1. The purpose of the present paper is to present the new data for "porphyroxine-meconidine" obtained on the United Nations opium samples, and to bring up to date, in the light of this additional information, our knowledge of the relation between the content of "porphyroxine-meconidine" and the origin of the opium.

2. The "porphyroxine-meconidine" is a minor alkaloid of opium which has the property of changing to a red-coloured compound when heated in dilute mineral acid. It is here given this double name because it has been known under both the names "porphyroxine" and "meconidine", while the quotation marks are used because the descriptions of its properties under these names were incorrect in both cases. The history of this alkaloid and some account of its true properties will be found in "The story of 'Porphyroxine-Meconidine', the red-turning alkaloid of opium", an article written simultaneously with this paper, and to be published in the Bulletin on Narcotics, Volume IV, No. 1 (1952). Some information on the true properties in addition to the red-turning characteristics was previously given in document E/CN.7/117, 14 April 1948, part II D, "Some Minor Alkaloids of Opium. Alkaloid 1, 'Porphyroxine-Meconidine'."

3. The Secretariat chemists have previously studied the relation of "Porphyroxine-Meconidine" to origin, using the opium samples then available. (Document E/CN.7/195, 26 March 1950, The Comparative Determination of "Porphyroxine-Meconidine".) The Canadian chemists C. G. Farmilo and P. M. L. Kennett, collaborating in the international opium research, also contributed a study on this subject, using most of the same opium samples (Document E/CN.7/207, 19 October 1950, Further data on "Porphyroxine-Meconidine".) These results were very promising.

4. The new data do not change the general picture, in particular the conclusions that the opium of India is usually especially high in "porphyroxine-meconidine" and that of Iran especially low. It has, however, been found that, although Turkish samples are usually intermediate, some are as high as most of those from India, and a few are very high. All but one of the very high Turkish samples

/were from

were from Zile or Malatya, thus showing a regional difference within the larger region of Turkey. Further discussion of results will be given after the new data, and curves for five of the main regions based on all available data, have been presented.

II. The Method

5. The method used to obtain a comparative colorimetric value for the "porphyroxine-meconidine" was virtually the same as previously given in document E/CN.7/195.

6. Rub 1.5 grammes opium and 1 gramme $Ca(OH)_2$ with 10 cc water to a smooth paste, in a mortar with a pouring lip, then add 50 cc water to the mixture in the mortar and stir frequently during 1/2 hour, getting as complete solution as possible. Filter and put 40 cc of the filtrate (taken as representing 1 gramme of opium) into a continuous extraction apparatus with peroxide-free ether. Extract until the ether coming over will no longer yield a red or pink color when a portion is evaporated on the steam bath in a small porcelain crucible with a few drops of (1:9) HCl. (It is best to stop the boiling while the test portion of ether is taken from the apparatus. The extraction takes about 3 hours with an efficient apparatus).

7. When the extraction is complete, pour the ether into an evaporating dish, rinsing the flask with a little methanol, and evaporate to dryness. Treat the residue with 10 cc 1 per cent HCl (1 per cent by volume of concentrated HCl) and heat on the steam bath, stirring the residue into solution with a glass rod. This develops the red colour. The solution may be evaporated to about 6 to 9 cc during this heating.

8. Pour the solution into a 10 cc graduate and rinse in with just the necessary amount of 5 volume-per cent ascetic acid to make up to 10 cc again. Mix and read the colour in the 1/8 inch cell of the Lovibond tintometer. When the colour is quite weak it may be read in the 1/4 or 1/2 inch cell; when it is very strong it may be read in the 1/16 inch cell, or the solution diluted with 5 volume-per cent acetic acid and then read.

9. After obtaining a reading, pour the solution into a test tube and reheat in the steam bath, cool, and read again. Repeat, if necessary, until the maximum red colour has been found. The colour is matched with the Lovibond red slides, if necessary using some yellow or blue slides. Only the red

/colour

colour value is taken as significant. If the reading is made in a larger or smaller cell than 1/8 inch, or the solution diluted beyond 10 cc, the result is calculated to correspond to the colour developed from 1 gramme opium, in 10 cc solution, read in the 1/8 inch cell. The tabulated results are all on this basis.

III. The United Nations samples

10. The new samples have been given to the United Nations for opium research, by China, France, for Laos and Vietnam, Greece, India, Iran, Korea, Turkey, the United States of America, and Yugoslavia. The sample from the Union of Soviet Socialist Republics listed hereafter was contributed by Laboratoires Clin-Comar, France; and the Iranian export samples by the Mallinckrodt Company, U.S.A.

11. The majority of the samples have been contributions from the producing countries of their own opium, for international distribution to chemists taking part in the opium research, as well as for study by the Secretariat. Some small samples are sufficient only for the Secretariat research. In most cases the large samples received from the producing countries each consisted of several separate lumps or loaves, for example, 4 separate lumps from Merzifon (Turkey No. 7) and 3 from Burdur (Turkey No. 8).

12. For the purposes of this study, each separate lump was run for "porphyroxine-meconidine"; the lumps in the same sample are distinguished as A, B, C, etc. In many cases there were some rather large differences between different lumps included in the same sample. Some of the large samples consisted of quite a number of small lumps or loaves. The majority of these were also run separately; they are distinguished as a, b, c, d, etc.

IV. "Porphyroxine-Meconidine" Values of United Nations Samples

CHINA

U.N. 37 - Received from Taiwan -	lump A	14.0
	lump B	13.5
	lump C	14.4
	lump D	10.5

/GREECE

GREECE

U.N. 25 - small loaf, a	12.0
- b	14.0
- c	13.0
- d	12.8
- e	9.2
- f	9.4
- g	10.0
- h	10.0
- i	11.6
- j	12.0
- k	12.0
- l	12.0
- m	10.4

INDIA

U.N. 34 - Banaras opium	34.6
U.N. 35 - Malwa opium	35.8
U.N. 36 - Excise opium	27.0

IRAN

U.N. 18 - Export opium	5.5
U.N. 19 - Export opium	4.2
U.N. 20 - Export opium	5.0
U.N. 21 - Export opium	4.4
U.N. 47 - Fars	7.0
U.N. 48 - Isfahan	5.6
U.N. 49 - Kerman	5.4
U.N. 50 - Kermanshah	16.2
U.N. 51 - Khorassan	9.0
U.N. 52 - Nehavand	15.3

KOREA

U.N. 16 - Korea No. 1 - A	1.2
No. 1 - B	2.5
U.N. 17 - Korea No. 2	11.6

LAOS

U.N. 26 - Laos, Luang Prabang, lump A	10.0
lump B	20.0
lump C	24.8
U.N. 27 - Laos, Xieng-Khouang, lump A	19.6
lump B	19.2

/TURKEY

TURKEY

U.N. 1 - Turkey No. 1 - Aydin -	lump A	24.4
	lump B	12.4
	lump C	17.2
	lump D	14.4
	lump E	16.4
	lump F	29.6
	lump G	22.0
	lump H	22.0
U.N. 2 - Turkey No. 2 - Afyon -	lump A	25.2
	lump B	18.0
	lump C	7.8
U.N. 3 - Turkey No. 3 - Corum -	lump A	13.0
	lump B	10.0
	lump C	29.6
	lump D	26.0
U.N. 4 - Turkey No. 4 - Cal -	lump A	12.8
	lump B	8.0
	lump C	7.2
	lump D	14.2
U.N. 5 - Turkey No. 5 - Usak -	lump A	10.8
	lump B	18.4
	lump C	21.0
	lump D	2.8
U.N. 6 - Turkey No. 6 - Nallihan -	lump A	32.0
	lump B	10.0
	lump C	11.2
	lump D	28.0
	lump E	12.0
U.N. 7 - Turkey No. 7 - Merzifon -	lump A	5.6
	lump B	9.0
	lump C	14.4
	lump D	14.8
U.N. 8 - Turkey No. 8 - Burdur -	lump A	5.3
	lump B	18.0
	lump C	7.8
U.N. 9 - Turkey No. 9 - Kula -	lump A	24.8
	lump B	23.9
	lump C	13.0
	lump D	23.4

/U.N. 10 -

U.N. 10 - Turkey No. 10 - Sandikli	lump A	14.0
	lump B	32.6
	lump C	10.0
U.N. 11 - Turkey No. 11 - Aksehir	lump A	15.2
	lump B	22.4
	lump C	44.0
U.N. 12 - Turkey No. 12 - Zile	lump A	16.8
	lump B	40.0
	lump C	64.0
	lump D	20.2
	lump E	31.0
	lump F	48.8
U.N. 13 - Turkey No. 13 - Isparta	lump A	15.0
	lump B	16.0
	lump C	8.4
U.N. 14 - Turkey No. 14 - Malatya	lump A	70.8
	lump B	41.2
	lump C	23.2
	lump D	72.0
	lump E	64.8
U.N. 15 - Turkey No. 15 - Export opium		11.6
U.N. 29 - Exhibition	A, half loaf	11.8
	B, whole loaf	10.0
U.N. 30 - Exhibition, standardized opium		12.4
U.N. 31 - Exhibition, reduced size cubes		13.6
U.N. 40 - Purchased at Eskiser		4.1
U.N. 41 - Purchased at Kutahya	ball-A	15.2
	lump B	8.0
U.N. 42 - Purchased at Afyon		3.2
U.N. 44 - Loaf in copper vessel		9.0

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U.N. 39 - Sample from France		10.0

/VIETNAM

VIETNAM

U.N. 28 - Tonkin, Laokay,	lump a	4.3
	lump b	20.2
	lump c	15.2
	lump d	13.8
	lump e	13.8
	lump f	16.4
	lump g	12.0
	lump h	37.0
	lump i	20.0
	lump j	18.4
	lump k	13.8
	lump l	14.4
	lump m	10.8
	lump n	16.4
	lump o	20.0
	lump p	21.0

YUGOSLAVIA

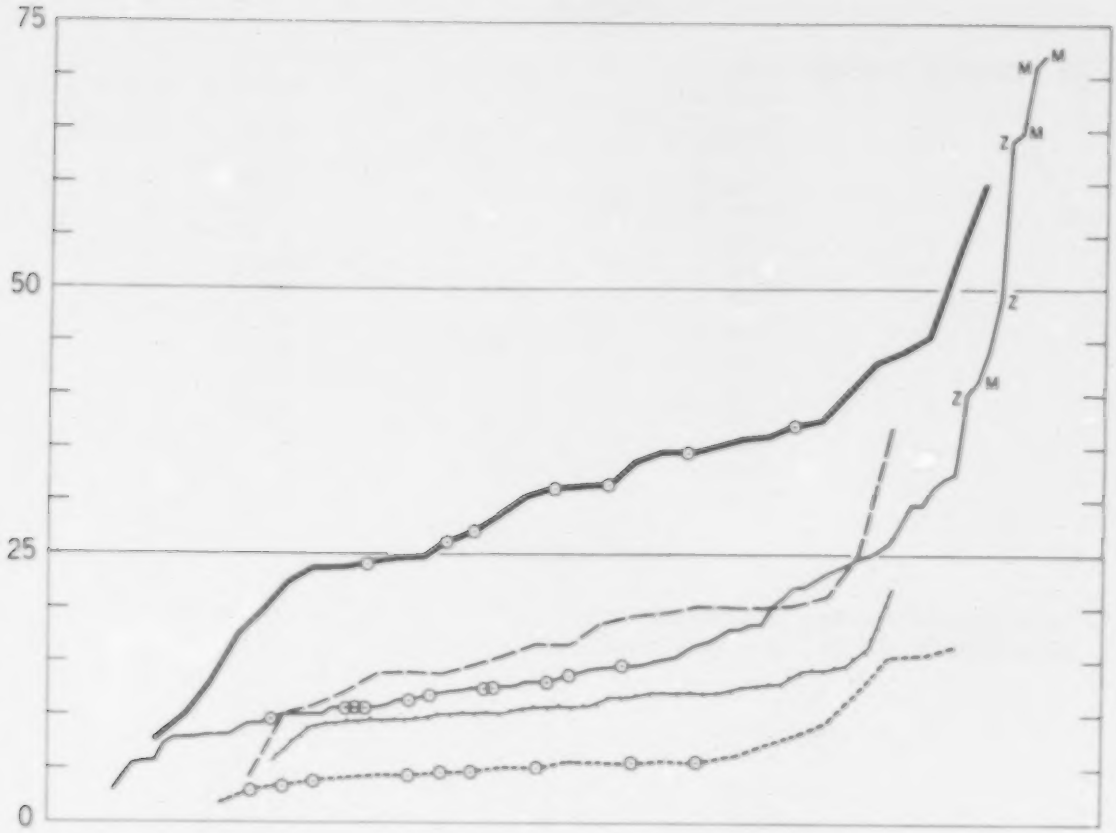
U.N. 24 - Yugoslavia No. 1 - Export type		12.4
U.N. 38 - Yugoslavia No. 2 - small loaf,	a	14.0
	b	16.0
	c	21.8
	d	10.8
	e	10.8
	f	10.8
	g	10.0
	h	19.6
	i	10.8
		10.8

V. Chart of "Porphyroxine-Meconidine" Values

14. The accompanying chart shows all the available data for five of the main regions of opium production, and shows the comparative results. The curves represent 88 samples from Turkey, 32 from India, 30 from Greece and Yugoslavia, 24 from Iran, and 21 from Laos and Vietnam. Horizontally, the samples are simply arranged in their order of value for each curve, and the values are spaced more widely the fewer the number of samples. The ordinates correspond to the colour values obtained on the various samples.

/Chart

COMPARATIVE "PORPHYROXINE-MECONIDINE" VALUES IN FIVE PRODUCING REGIONS



Turkish samples are spaced 1 unit apart, Yugoslavia and Greece 2, India 2 1/2, Iran 3, Laos and Vietnam 3.

Turkey - 88 samples, Yugoslavia and Greece - 30, India - 32, Iran - 24, Laos and Vietnam - 21.

Ordinates correspond to the colorimetric "porphyroxine-meconidine" values.

Circles indicate samples of export opium of India, Iran, and Turkey.

"Z" and "M" indicate samples from Zile and Malatya (Turkey).

VI. Facts and Conclusions from all the Data

15. Conclusions must be based, not merely on the new data, but on all the available data. The chart given in paragraph 14 shows the comparative values for all samples thus far available from five of the principal producing regions. The generally high trend of values for samples from India, and the generally low trend of values for samples from Iran, are clearly apparent. Some of the Turkish samples are high and a few are very high, but in general the samples from Turkey, as well as most of those from Greece and Yugoslavia, and Laos and Vietnam, have intermediate values. Most samples from other countries, not shown on the chart, are also in the intermediate range. The specific values for all the earlier samples will be found in document E/CN.7/195.

16. Export samples of India, Iran and Turkey are marked on the curves with circles. The export opium of Turkey is made by mixing all the opium of the country, and thus in itself represents the average of Turkish opium. The export samples of Turkey fall almost entirely on the lower half of the curve for Turkey as represented here. The significance of this is that in obtaining representative samples of different types, the varieties of Turkish opium containing high "porphyroxine-meconidine" have been over-represented, in comparison with the quantity of production. The Turkish export samples (values 9.4 to 14.4) indicate virtually the same curve as found for Balkan opium (Greece and Yugoslavia). This is to be expected for Turkish "druggist" opium, which constitutes the chief production of the country and is known to be quite similar to Balkan opium.

17. The "porphyroxine-meconidine" values may be broadly divided into four zones: low, up to 8; intermediate, 8 to 22; high, above 22; very high, above 34. The main part of the curse for Iran is below the value 8; the main parts of the curves for Greece and Yugoslavia, Laos and Vietnam and Turkey, (as well as the values for most other countries whose samples have been tested), are between the values 8 and 22; the main part of the curve for India is above the value 22. A significant part, though not the main part, of the Turkish curve is still above this value, and also a very few scattered values from other countries.

18. About one-third of the curve for India is in the "very high" zone, above the value 34. Also a few samples from Turkey rank with, or even above, the highest of the Indian samples: all but one of these were from Zile or

/Malatya,

Malatya, thus showing a regional difference within the larger region of Turkey. The one other Turkish sample having a very high value was from Aksehir (value 44.0). Only two samples neither from India nor from Turkey have been found so far with values above 34: one of these was from Vietnam (Tonkin, value 37.0) and the other (value 67.2, not shown on the chart) was from Japan, where opium is no longer produced.

19. The Indian and Iranian opiums are in several respects quite similar, but in "porphyroxine-meconidine" values they are almost always entirely different. In determining the origin of contraband opium this test is valuable, especially in distinguishing Indian and Iranian opiums from each other, and to some extent in distinguishing either Indian or Iranian opium from most other kinds. The possibility of a sample with a very high value being Turkish rather than Indian, and the possibility of a very low value resulting from adulteration or the inferior grade of a particular opium rather than indicating Iranian origin, should always be kept in mind. In the latter case the ratio of "porphyroxine-meconidine" value to morphine percentage may mean more than the "porphyroxine-meconidine" value taken alone.

20. The "porphyroxine-meconidine" colour reading is very valuable in determining the origin of seized opium, but it cannot be decisive in itself. It must be considered in conjunction with other tests, or in connexion with the facts and circumstances of the seizure. Rightly used, it is one of the best tests for the chemical determination of origin. The different positions of the curves for various countries, and in particular the consistent differences between the export opiums of India, Iran and Turkey are eloquent of the relation of "porphyroxine-meconidine" value to origin.